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ELECTROCHEMISTRY RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY
JOHN SCHOFF MILLIS SCIENCE CENTER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO 44106

Semi-Annual Status Report No. 6

1 October 1974 to 31 March 1975

CATALYSTS FOR ELECTROCHEMICAL GENERATION OF OXYGEN

Report Prepared by: W. E. O'Grady and J. Huang

Project Director: Ernest Yeager

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA-Ames Grant Nos. NGR 36-027-050
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CATALYSTS FOR THE ELECTROCHEMICAL
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Sponsor: NASA-Ames

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I. PRIMARY OBJECTIVES

1. To find new, more effective catalysts for the electrolytic evolution of oxygen and to understand the mechanism and kinetics for the electrocatalysis in relation to the surface electronic and lattice properties of the catalyst, as well as developing an understanding of the structural features of the electrocatalysts which are critical to high electrochemical activity for the anodic generation of O_2 .
2. To evaluate the kinetics and mechanism of anodic generation of O_2 under well defined conditions in relation to the properties of the electrode surface.

II. SPECIFIC OBJECTIVES FOR THIS REPORTING PERIOD

1. Kinetics and mechanism of oxygen evolution on platinum metal in hydrofluoric and sulfuric acids including the effects of foreign anions.
2. Development of the LEED-Augur-thin layer electrochemical system for the examination of electrocatalytic surfaces.
3. Preparation and examination of samples for electrocatalytic LEED-Augur studies.

III. SUMMARY OF THE WORK

1. Kinetics and mechanisms of oxygen evolution on platinum.

Previous work has indicated that cation and anion additions can have significant effects on the oxygen evolution kinetics on platinum. An effort has been made here to study these effects and their inhibitive or catalytic nature.

We previously reported⁽¹⁾ an anomalous behavior of the growth of the

oxide on Pt in the presence of CsF added to the HF solution. It has subsequently been found that the CsF was contaminated with Cl^- which gave rise to the reported behavior. As a result of this finding, we have investigated the effect of adding Cl^- to the HF solution. Figure 1 shows the cyclic voltammogram of Pt in pure HF. Chloride is added to the HF solution in the form of HCl holding the concentration of F^- constant. The effect of 10^{-2} M Cl^- on the growth of the Pt oxide is seen in Figure 2. A comparison of Figures 1 and 2 indicates that the Cl^- is strongly adsorbed retarding the growth of the Pt oxide. Below 10^{-5} M Cl^- no perturbation of the oxide growth can be detected in the cyclic voltammogram. However, the Tafel behavior for O_2 evolution is quite different from that in pure HF and this is being investigated further.

A set of experiments similar to those of the Cl^- in HF were run adding H_2SO_4 to the HF. The results are quite surprising. Again the concentration of F^- was kept constant as the $\text{SO}_4^{=}$ was added to the HF in increasing concentrations. The addition of the $\text{SO}_4^{=}$ perturbs the cyclic voltammogram greatly (Figure 3). In the initial region of oxide growth it is seen that the $\text{SO}_4^{=}$ is sufficiently strongly adsorbed that the initiation of the oxide formation is pushed to a higher potential similar to the situation observed with Cl^- . If the potential of the initiation of oxide growth is plotted against the $\log [\text{SO}_4^{=}]$ a linear plot is obtained with a slope of 15mV per decade of $[\text{SO}_4^{=}]$ concentration (Figure 4). When the concentration of H_2SO_4 in HF reaches 0.1 N the behavior is identical to that of pure $0.1 \text{ N H}_2\text{SO}_4$. The portion of the cyclic voltammogram in the hydrogen adsorption region also is quite interesting. Conway (2) has postulated from his cyclic voltammetry studies of Pt in very pure H_2SO_4 that the four peaks observed in the hydrogen region are characteristic of a clean solution. In the results for HF we do not find four peaks in the hydrogen region (Figure 1). Upon

the addition of $2 \times 10^{-3} \text{ N SO}_4^{=}$ four peaks begin to emerge in the hydrogen region (Figure 3). These results indicate that there is a large contribution of the $\text{SO}_4^{=}$ ions to the structure in the hydrogen adsorption region. There now seems to be a question as to the validity of the four peak structure as a criteria of solution purity.

There does seem to be a larger current in the double layer region for the HF solutions containing $\text{SO}_4^{=}$ which might be attributed to the adsorption of HF molecules or HF_2^{-} ions. In order to check this postulation HF was added to $0.1 \text{ N H}_2\text{SO}_4$. Prior to the addition of HF the cyclic voltammograms for $0.1 \text{ N H}_2\text{SO}_4$ were run. This solution of H_2SO_4 was prepared using Ultrapure H_2SO_4 and pyrolyzed H_2O . The pyrolysis was carried out in a system similar to the one described by Conway (3). The voltammograms obtained in this solution exactly duplicate the work of Conway (2). Previous experiments using triply distilled H_2O and reagent reagent grade H_2SO_4 could not reproduce the results published by Conway. Further work indicated this discrepancy to be due to impurities in the H_2SO_4 . When the HF was added in varying concentrations up to 10^{-1} N F^{-} , no change was detected in the double layer regions of the cyclic voltammograms. Thus we conclude that the $\text{SO}_4^{=}$ which is adsorbed even in the hydrogen region is not affected by the addition of the HF.

The effects of the addition of Cl^{-} to the H_2SO_4 solution were also studied. Again quite dramatic changes were found upon the addition of the Cl^{-} . Both the hydrogen and oxygen regions were affected indicating that the Cl^{-} has the ability to displace some of the adsorbed $\text{SO}_4^{=}$ and hence change the cyclic voltammogram drastically. The actual effects of the Cl^{-} on the kinetics of O_2 evolution are now understudy.

A comparison of solutions of HF and H_2SO_4 of equal pH was made. According to Frumkin et al. (4) a 0.14 N HF and $0.04 \text{ N H}_2\text{SO}_4$ have the same

pH. These solutions were made and the cyclic voltammograms on Pt were run. The results are shown in Figure 5. Here it is seen that the behavior of Pt in these two solutions is dramatically different. In the H_2SO_4 the initiation of the oxide growth is at a higher potential than in the HF solution evidently due to the adsorption of $\text{SO}_4^{=}$. Again the four peak pattern is found in the hydrogen region in the H_2SO_4 solution where as in the HF solution a pattern with only three peaks is found and these not being very well defined. These data again indicate that the $\text{SO}_4^{=}$ plays a strong part in the development in the pattern in the hydrogen region in the cyclic voltammogram.

2. Development of the LEED-Auger-Thin-Layer Electrochemical System

The development of a rationale basis for electrocatalysis requires information concerning the composition and geometric structure of the surface. In an effort to understand the contribution the atomic structure makes to electrocatalysis we are combining an electrochemical thin layer cell with an ultra-high vacuum system containing a LEED-Auger spectrometer. The Auger technique identifies the elemental composition on the surface as well as giving the relevant information on the valency states, LEED gives the geometric ordering in the surface with will allow us to relate the surface structure to catalysis.

The progress in the assembly of the entire system has been held up because the components (valves and feedthroughs) which have been on order now for some six months have not been delivered. However, during this interim we have constructed a thin layer electrochemical cell and have begun obtaining data with it. The particular thin layer cell which we expect to utilize in conjunction with the LEED-Auger system has been designed and is in the process of being built in the machine shop. The techniques involved in using a thin layer cell require some experience and we are at present developing these techniques.

The sample transfer mechanism for introducing the electrodes into the vacuum system as well as in transferring them from the sample preparation chamber to the LEED-Auger chamber has been designed and built and is shown schematically in Figure 6. Our transfer system will maintain the electrodes at temperatures near liquid nitrogen temperature (100K) during the transfer.

The reaction chamber and the associated ion and titanium sublimation pumps have been assembled in the laboratory and pumped down to a pressure of 9×10^{-9} torr. Some difficulty has been experienced in obtaining a lower vacuum with this system. We believe this is due to a contamination and appropriate steps have been taken to alleviate this problem.

3. Preparation and Examination of Samples for Electrocatalytic LEED-Auger Studies

Ruthenium oxide (RuO_2) supported on a titanium substrate which was found to be one of the more effective electrocatalysts in the earlier phases of this NASA-supported research continues to be of great interest. In order to develop techniques for sample preparation which are critical for the LEED studies and to obtain experience in the utilization of the instrumentation, preliminary LEED-Auger experiments have been undertaken on the gas phase oxidation of single crystal ruthenium metal.

The Ru single crystal has been oriented to $\pm 1/2$ degree of the $11\bar{2}0$ direction, cut, polished and mounted in the LEED-Auger system. After some preliminary cleaning (heating to 600°C), the Auger spectrum shown in Figure 7 was obtained. No LEED pattern could be obtained from this surface. After heating the sample to 1000°C and extensive argon ion bombardment, the Auger spectra characteristic of the clean Ru surface as shown in Figure 8b can be obtained. Further removal of sulfur is achieved by heating to 1200°C and can be seen by comparing Figure 8a and 8b. The LEED pattern for the clean $11\bar{2}0$ Ru surface has been obtained and is shown schematically in Figure 9a. If this

clean surface is then exposed to oxygen at a pressure of 8×10^{-9} torr, the LEED pattern shown schematically in Figure 9b develops. If the oxygen pressure is increased these new spots disappear and the original clean surface spots become decreased in intensity.

In order to develop reference Auger spectra for comparison to the RuO_2 catalysts, the single crystal surface has been oxidized in 10^{-5} torr O_2 at 450°C and then observed using Auger. The $M_{vN_{4,5}N_{4,5}}$ Ru Auger line for the oxide shows a shift of about 1 eV from the **same line for Ru metal**. This observation agrees with the data which we obtained previously using x-ray photoelectron spectroscopy (XPS) (5).

A second sample which is being prepared is a gold single crystal. This material, which is much softer than Ru, cannot be mechanically polished but must be electropolished. The polishing of this sample has proven to be quite difficult and only one acceptable sample has been prepared.

IV. PROJECTED WORK

Research during the up-coming six months will include the following:

1. Electrochemical characterization of catalysts.

The work on the effects of cation and anion addition to the electrolyte on the kinetics of O_2 evolution will be continued and the effects in basic solution will also be studied.

We plan to continue the work on RuO_2 single crystals. This will be possible because we have obtained access to the correct type of furnace for growing the single crystals.

2. Structural studies of electrocatalysts.

During the up-coming period, we plan to finish the Ru oxidation experiments including the LEED and Auger characterization.

The electrochemical portion of the LEED-Auger-thin layer electrochemical system should be completed by September. Preliminary experiments utilizing this complete system should be under way shortly thereafter.

V. PROJECT PERSONNEL

Jerry Huang, Graduate Student

William E. O'Grady, Postdoctoral Research Associate

Ernest Yeager, Professor of Chemistry, Project Director

REFERENCES

1. Semi-Annual Status Report #5, 1 April 1974 to 30 September 1974, Catalysts for Electrochemical Generation of Oxygen, W. O'Grady and E. Yeager, NASA-Ames Grant No. NGR 36-027-050.
2. B. E. Conway, H. Angerstein-Kozłowska, W. B. A. Sharp and E. E. Criddle, Anal. Chem., 45, 1331 (1973).
3. H. Angerstein-Kozłowska, B. E. Conway and W. B. A. Sharp, J. Electroanal. Chem., 43, 9 (1973).
4. B. I. Poblovchenko, N. A. Epshtein and A. N. Frumkin, J. Electroanal. Chem., 53, 95 (1974).
5. Semi-Annual Status Report #4, 1 October 1973 to 31 March 1974, Catalysts for Electrochemical Generation of Oxygen, W. O'Grady and E. Yeager, NASA-Ames Grant No. NGR 36-027-050.

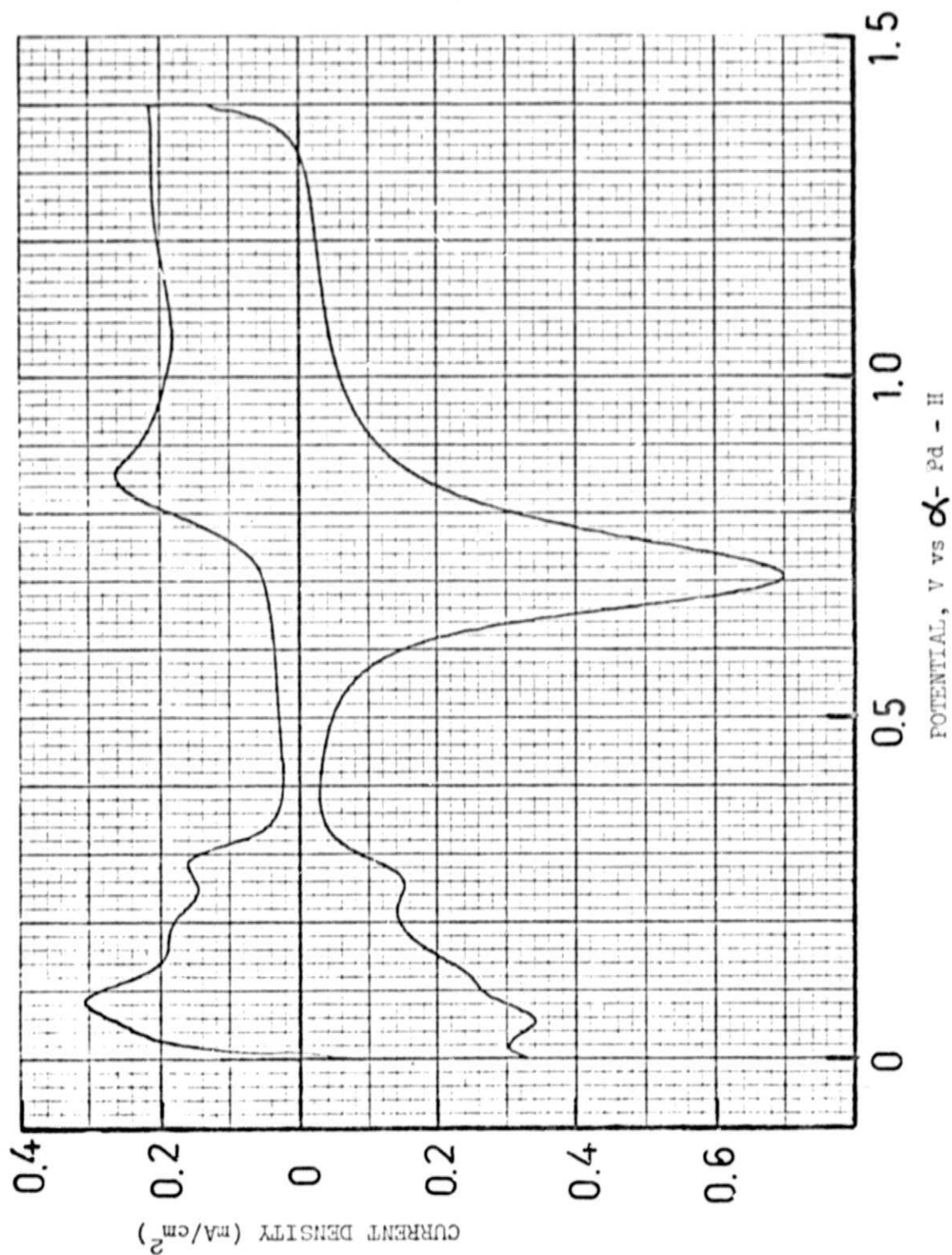


Figure 1. Cyclic voltammogram of Pt with a sweep rate of 100/mV sec. Electrolyte: 0.1N HF.

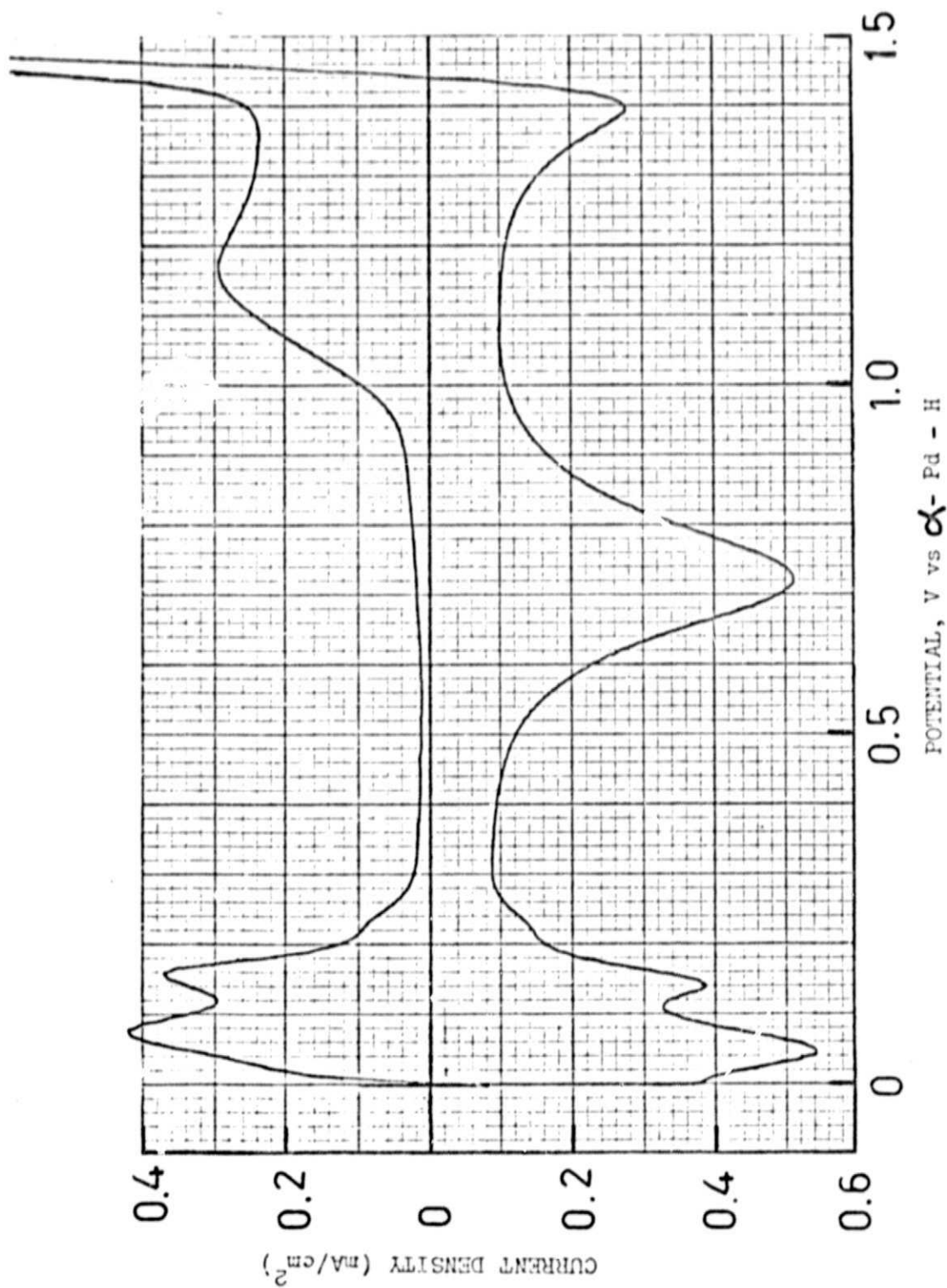


Figure 2. Cyclic voltammogram of Pt with a sweep rate of 100/mV sec. Electrolyte: 0.1N HF with 10^{-2} N HCl added.

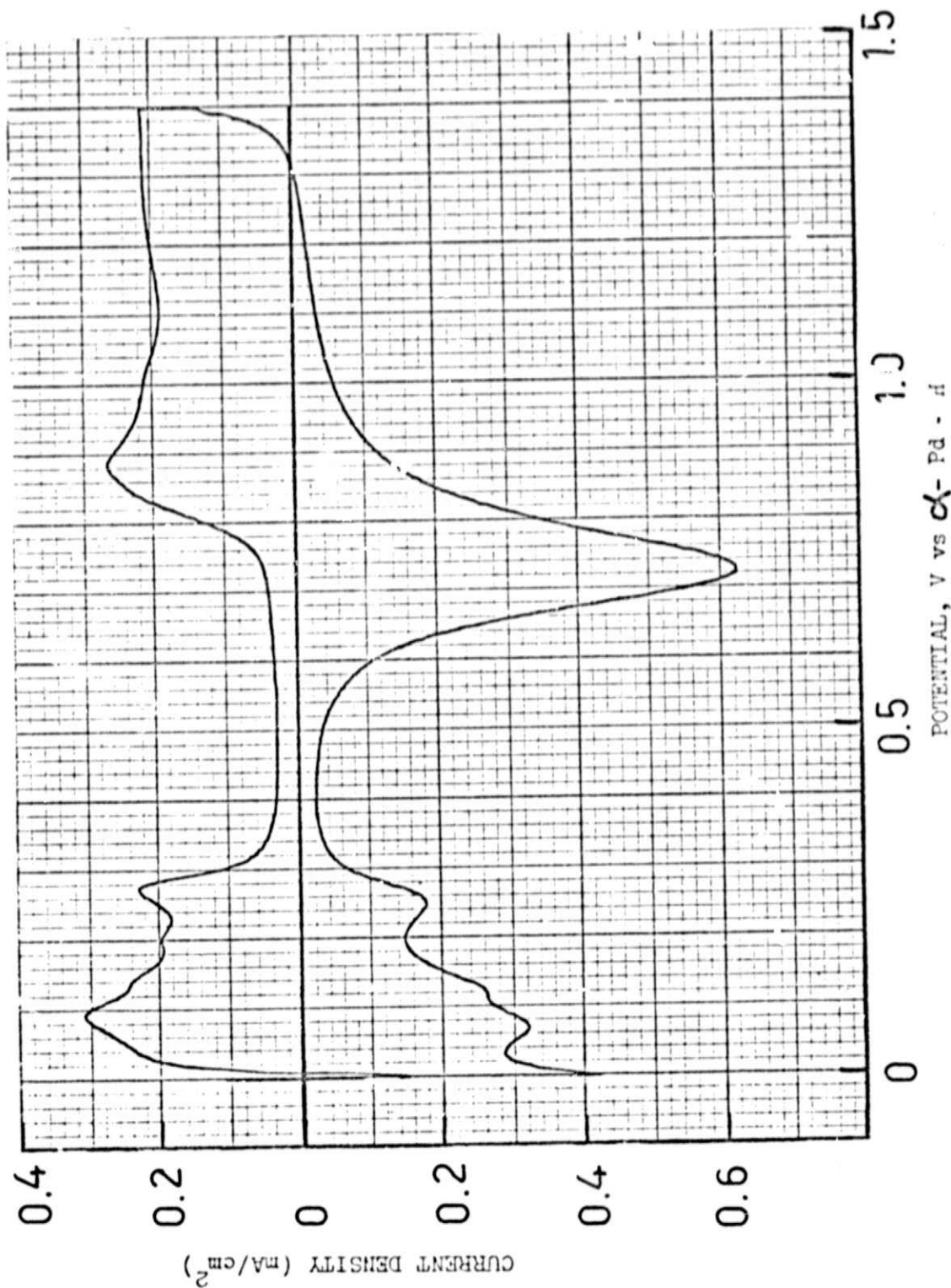


Figure 3. Cyclic voltammogram of Pt with a sweep rate of 100/mV sec. Electrolyte: 0.1N HF with 10^{-2} N H_2SO_4 added.

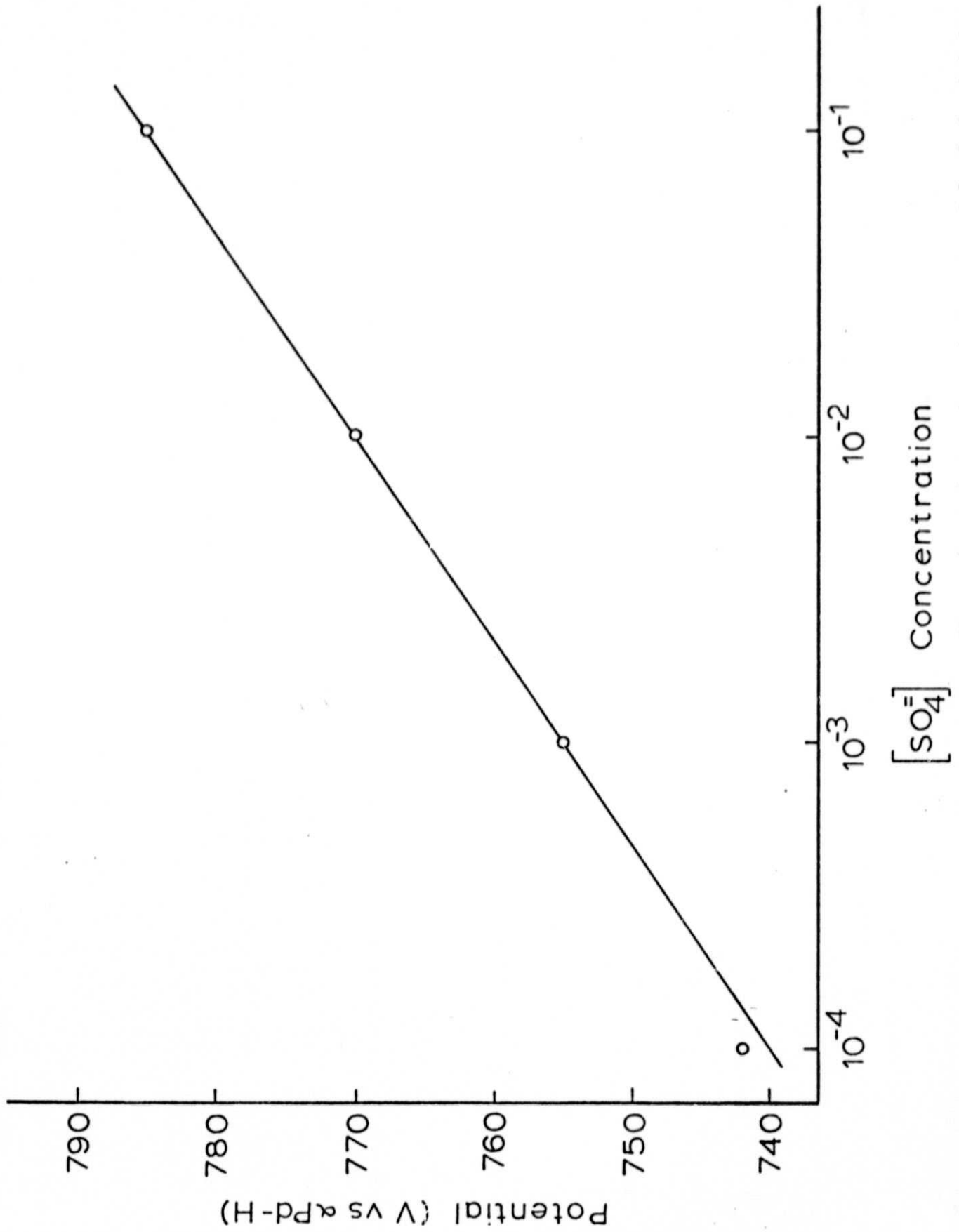


Figure 4. Relationship of the potential of the initiation of oxide growth with the log of the $\text{SO}_4^{=}$ ion concentration.

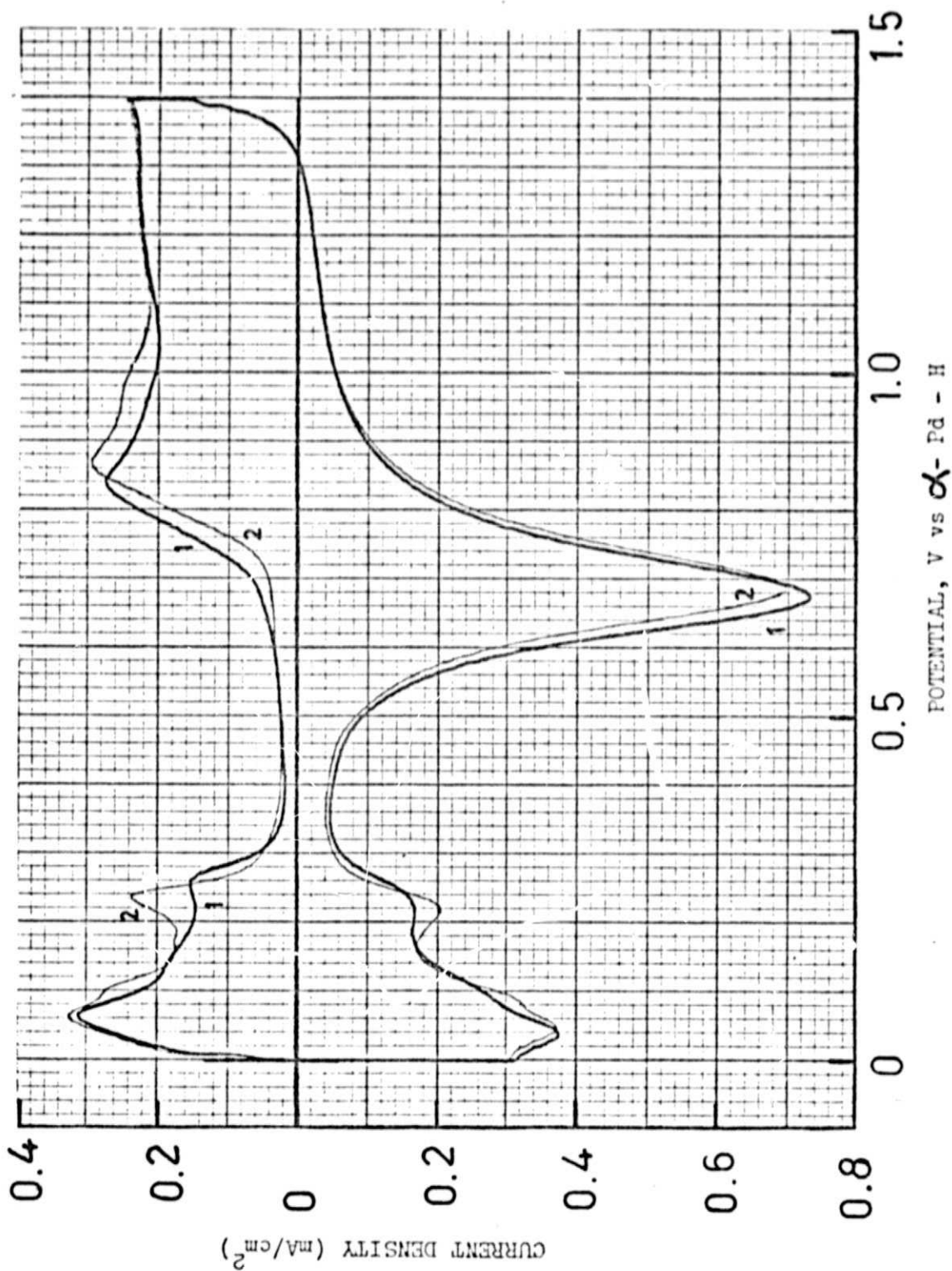
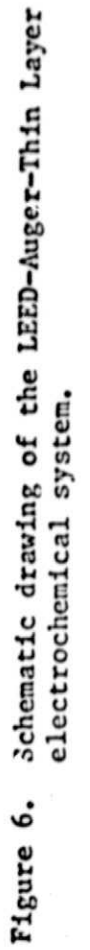


Figure 5. Comparison of the cyclic voltammograms of Pt at a sweep rate of 100 mV/sec.

- 1) 0.14 HF
- 2) 0.04 H₂SO₄



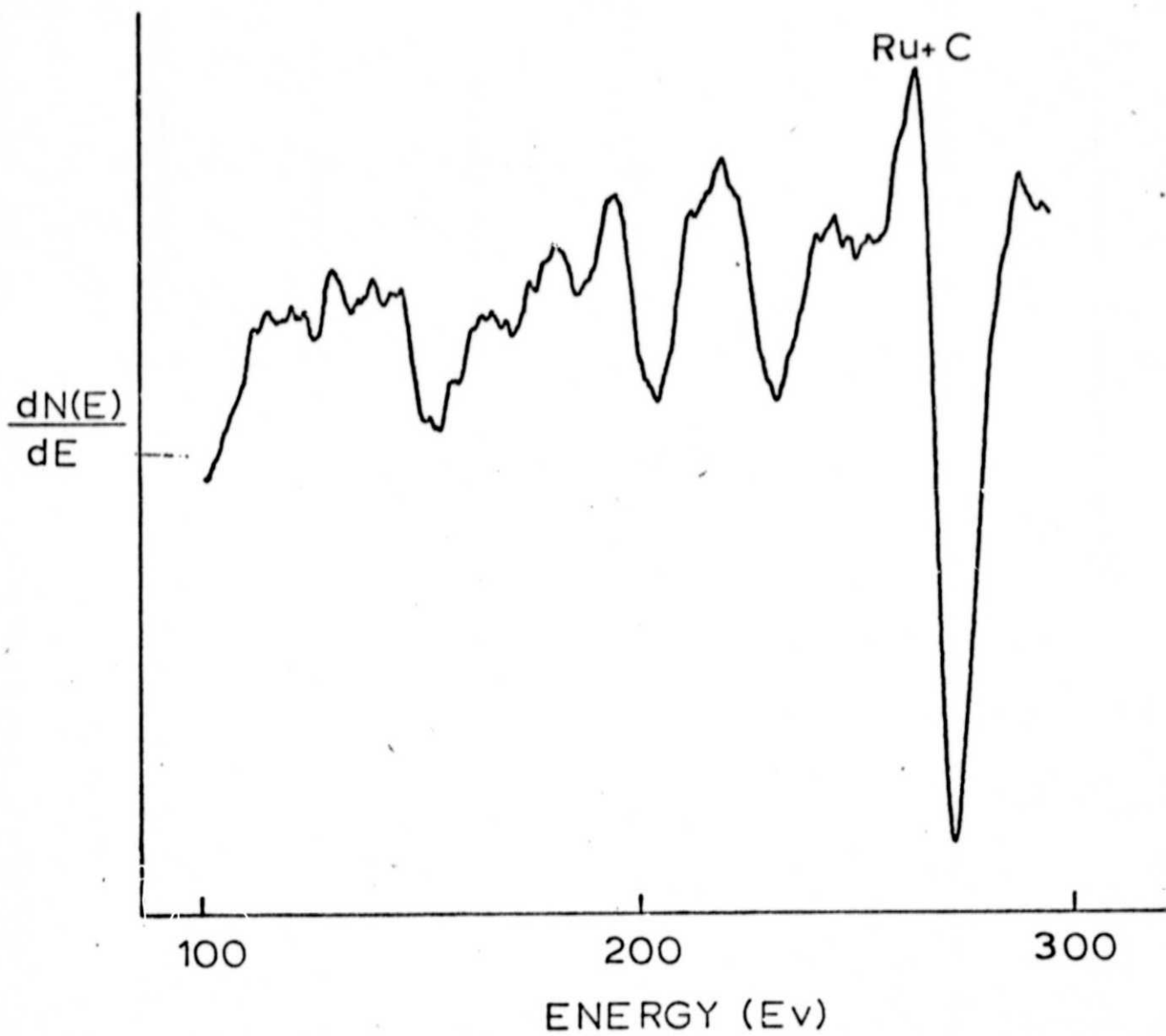


Figure 7. Auger spectrum of a partially cleaned Ru (1120) surface (heated to 600° C).

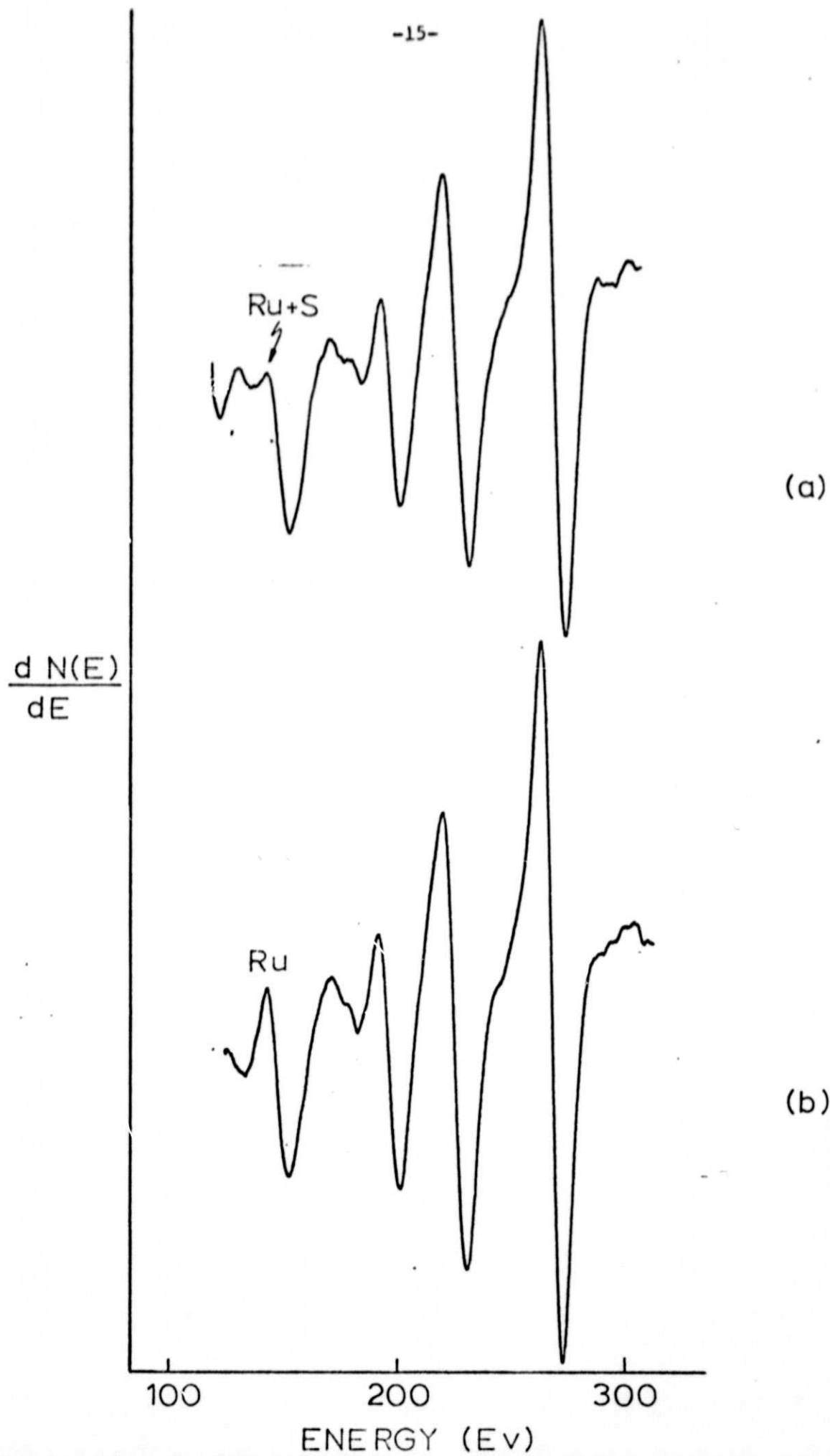


Figure 8. Auger spectra of a cleaned Ru (11 $\bar{2}$ 0) surface
a) Argon ion sputtered and heated to 1000° C.
b) Argon ion sputtered and heated to 1200° C.



(a)



(b)

Figure 9. Schematic LEED Patterns of Ru (11 $\bar{2}$ 0)
a) Clean surface corresponding to the Auger spectrum shown in Figure 8b.
b) Initial oxidation of the clean Ru (11 $\bar{2}$ 0) surface x's indicate new spots.